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FROM

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ATTN

Alice Furst

RE

Director Comments

DATE _____

28 June 1988

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PETER KEPLER LETTER Notes (March 22, 1988)

- P.1 2nd paragraph: "Based on universally applicable geochemical reactions..." The reactions used in the Angino report are idealized thermodynamic equilibrium pure end member reactions that do not directly relate to "naturally elevated background levels of metals and other parameters" prior to mining activity in the Galena subsite. The reactions are based on pyrite instead of the predominant marcasite as the acid providing sulfide, assume a much higher pyrite (iron sulfide) fraction than is present, and ignore the effect of secondary mineral formation, adsorption, and surface area characteristics in fractured silica to carbonate host rocks that more properly define the natural levels of metals in the water systems in the Galena subsite.
- P.2 2nd paragraph "natural background conditions alone can account for the elevated metals levels." Natural background conditions range from background (no sulfide mineralization) threshold (peripheral sulfide mineralization) and ore zone (ore grade mineralization). The range of concentrations produced by conditions today can be estimated statistically but are not definable by the idealized laboratory thermodynamic equilibrium modeling of the Angino report. Field conditions are more complex and are not predicted adequately by this modeling technique, which can be used to check for dissolution or precipitation tendencies of selected mineral species.

"PREMINING SURFACE AND SHALLOW GROUNDWATER QUALITY
IN THE VICINITY OF SHORT CREEK, GALENA, KANSAS"
BY ERNEST E. ANGINO CONSULTING GEOCHEMIST

Review by Richard K. Glanzman, Geochemist, CH2M HILL

The comments are ordered by chapter, page, and paragraph number.

CHAPTER 1

P.1 1st paragraph, 8th line. "A comparison of the effects of a sulfide ore body on water quality at Galena."

Issue: Premining water quality

Comment: Since premining conditions are undocumented, the affects should be considered potential.

2nd paragraph, 3rd line, "what must have existed" should more properly be what may have existed. There is little reason to believe the calculated concentrations must have existed over geologic time since the formation of the ore body.

6th line. "measured in unmined" perhaps but potentially affected by nearby mining activity.

8th line. What is meant by "A conservative approach was used in all computations and comparisons presented"? A truly conservative approach would have included rates of reaction, all secondary minerals, and adsorption. This all inclusive methodology was not used.

12th line. The surface and shallow groundwater quality may not have been "pristine" in the sense that the water may have contained certain concentrations of metals but these concentrations can be compared with the standards regardless of source or condition of the ore body.

14th line. The author should document the "similar (known) present day sulfide ore bodies in other localities" to facilitate our comparison of the mineralogy and water quality. Later in the report, the author uses only the Red Dog example which we do not acknowledge as being comparable.

p.2 1st paragraph, Approach 4

"based on the natural laws of geochemistry" is a presumptuous statement. Geochemists have been able to define an equilibrium concentration of a particular element for a particular compound or mineral at a particular temperature, pressure, and to some extent other dissolved ions over essentially infinite time using laws of thermodynamics. How well this correlates to natural laws or even natural system conditions is subject to much debate among geochemists.

p.2 Approach 5--Not many springs in the Cherokee County area can be proven to be parts of the regional hydrologic cycle (system). Most, if not all, are parts of the local hydrologic system. Springs are part of the hydrologic system.

p.3 The boundaries of the Galena subsite in Figure 1 are shown as the City of Galena boundary. Is this a correct definition of the boundaries for what is being described in the text? The boundary does not correspond to the OUFS boundary. The author should clarify the boundary for his discussion.

p.4 3rd line, "published data of the era." Any data are developed against a socioeconomic framework of that era and its analytical abilities. They may or may not be a "clear indication" of what conditions were. We know of no quantitative net chemistry methods of this era that could adequately characterize the water quality.

p.4 1st full sentence. It is not possible to "predict likely concentrations of zinc, lead, and other ions present in solution" with reliable accuracy at any time from the natural water chemistry using only computer modeling techniques of equilibrium. A tendency or affinity for solutioning may be possible.

P.4 2nd full sentence. What level of "reasonable certainty and confidence" is believed concerning the results of "acceptable modeling codes, and appropriate thermodynamic data?" The author needs to define acceptable and appropriate.

p.5 1st full paragraph, 3rd line, "What must have existed in the water of the Galena, Kansas area during pre-mining time." This is presuming that equilibrium (or near equilibrium) thermodynamics calculates the existing concentration of a metal ion at "that time" but an equilibrium (or near equilibrium concentration) is a constant (or near constant). The concentrations of metallic ions in both surface and shallow groundwater

changes with at least seasonally and even hourly and daily in the case of surface water. The calculated equilibrium (or near equilibrium) concentration is actually a potentially maximum concentration for the given model conditions. Even in the case of the worst quality mine shaft water at Cherokee County, the metals are below the calculated equilibrium "concentrations." The equilibrium concentration approach is biased toward high concentrations, does not include potential limiting factors, and is therefore inappropriate to use in defining premining dissolved metal concentrations in either surface or groundwater.

p.10 Line 10. It was both milling and smelters that increased interest in mining the zinc ore.

p.10 Line 16. The author assumes without demonstration that southwestern Missouri is "geohydrologically similar." The referenced citations for this Missouri area refer to ore deposits not geohydrologic conditions.

CHAPTER 3

p.17 2nd Paragraph, 1st sentence. Baily (p. 304 to 306) reports only one spring in the Baxter Springs area as "Iron Spring," the second spring is "Baxter Spring No. 5, Newhouse Spring." Furthermore, he includes them in a "special group" involving lithium, boric acid, barium, etc., and not in the "Sulfide," "Sulfate," or "Chalybeate (iron) Group."

p.17 2nd paragraph, 2nd sentence. Bailey is misquoted on p. 324. What he states is "Cave and Chico springs, in the neighborhood of Galena, are located in the sub-Carboniferous strata and draw their waters from the highly fissured limestone and chert formations, which are so productive of lead and zinc in Kansas and Missouri." Furthermore on p. 313 he says that Cave Spring "furnishes one of the best waters that can be obtained for domestic purposes."

P.17 2nd paragraph, 5th sentence. The authors statement that sulfate concentration of 65 mg/l is high and is made without reference to a "low" or "normal" value. Even the deep aquifer (Roubidoux) contains as much sulfate as this in the Galena area.

P.17 2nd paragraph, last sentence. "The presence of iron and sulfate are "not" clear indications of mobilization and dissolution (sic) of the key elements from the county rock," underlining by reviewer. Why are these two parameters considered key? They are clear indicators that, somewhere in the flow path, conditions are such that iron and sulfate can be dissolved and transported.

There are other important causative mechanisms for mobilization of metals from mineralized deposits.

- P.18 2nd paragraph, 1st sentence. Haworth (1904), in the same paragraph, he also states that "Brilliant-faced crystals of galena" are found almost covered by minute grains of quartz and that "brilliant galena crystals" are partially covered with calcite and sand-like masses that are apparently still forming. These statements imply that at least some galena is protected from ground-water dissolution and also that the groundwater was not acidic (or the calcite would have been dissolved) in premining time. It, therefore, does not "clearly indicates that the groundwater had to be charged with lead and zinc."
- P.18 2nd paragraph, 2nd sentence. This quote ascribed to Haworth (1904) p. 85 cannot be found on that page. Part of the quote is found as part of a sentence discussing the large masses of flint ("along Short Creek valley between and Empire and Galena,") but there is no reference to ore. Later in the paragraph, he mentions zinc ore in the subsurface essentially interbedded with flint. Nowhere does Haworth say that "the area" (along Short Creek Valley)" is filled with ore."
- P.18 2nd paragraph, 3rd sentence. Where is it documented that "Short Creek flowed over the surface exposure of a sulfide ore body"? It is not clear that surface water "had to be passing over and through a slightly oxidized ore body." It was stated earlier that ore was discovered not at the surface but in a well. If ore outcropped it is difficult to believe it would not have been discovered by early prospectors.
- p.18 & 19. The mineralization may have contributed "trace" concentrations of zinc to "these waters" but lowering the pH to below 6 and mobilization of lead and cadmium has not been documented in these early reports.
- p.19 1st paragraph, 1st full sentence. "The local waters of the Galena site (sic) must clearly have been carrying cadmium, zinc, and possibly low concentrations of Pb (sic) in solution." requires documentation. Only "traces of zinc" is documented in the earlier literature.
- P.19 1st paragraph, 3rd full sentence. The "exposed ore" occurrence has not been documented. Also "rather high" sulfate in the surface and groundwater of the area needs quantification. Bailey (1902) chemical analyses of "local springs" does not bear out the conclusions

- stated in the paragraph. Unmined ore would likely have smaller surface areas for chemical reactions.
- P.19 1st paragraph, last sentence. The occurrence of "anglesite coatings on rocks of mineralized areas" does indicate that oxidation conditions existed as it does in all shallow depths of the earth's surface. However, it also indicates that lead sulfate is not very soluble and, therefore, implies that little of the lead from the oxidation of the galena was mobilized into the surface and groundwater during premining time.
- P.19 2nd paragraph, 1st sentence. We cannot find documentation that Short Creek flowed over outcrops of ore and would like a citation.
- P.19 2nd paragraph, 2nd sentence. Like the above comment. Please reference a report of location where "oxidized minerals found in the creek bed." If oxidized minerals are found in the creek bed, they would imply that the associated metals are both not very soluble and not very mobile.
- P.19 2nd paragraph, 4th sentence. The lead and zinc may become hydrated but do not have to go into solution. They can be retained at the metal sulfide crystal face as a secondary oxidation product that retards further oxidation of the metal sulfide.
- P.19 2nd paragraph, last sentence. Although anglesite is mentioned in the first paragraph on this page, it is ignored in the reaction in favor of cerussite. Should not lead sulfate be precipitated first? Then perhaps subsequently be altered to lead carbonate? Each of these processes and the minerals would retard further oxidation of galena.
- P.20 1st sentence. Sulfuric acid is not produced in the oxidation of sphalerite and probably not with galena. Sulfuric acid is created by the oxidation of pyrite and to a lesser extent by marcasite. It is doubtful that oxidation of sphalerite and/or galena "leads clearly to further acid chemical reactions and a definite reduction of pH (ph <7) in the containing waters."
- P.20 1st paragraph under Surface Water, 1st sentence, "higher concentrations of sulfate, heavy metals (zinc, cadmium, and lead), and excess acidity in surface and shallow groundwaters (sic) during premining time." The author needs to provide a reference point for reference of the concentrations of metals and acidity.

- P.20 1st paragraph under Surface Water, 2nd sentence. The possibility of a rising and falling water table "clearly" leading to alternating oxidizing and reducing conditions in the shallow subsurface is not clear. What depth is being discussed? How or why would the change of the shallow aquifer water table level change the oxidation/reduction potential? What documentation is provided that either change occurred?
- P.20 1st paragraph under Surface Water, last sentence. Think a word is missing in the latter part of the sentence. Such reactions, if they can be proven to have happened, may have led to a mobilization of selected trace metallic elements.
- P.20 Last sentence. We do not concur that the "facts" have not been demonstrated "beyond reasonable doubt." See the above and subsequent comments and questions.
- P.21--Item 1. This occurrence has not been documented to be true.
- P.21--Item 3. These reactions may have mobilized selected elements into solution but are not defined by individual solubilities alone. Formation of secondary minerals, adsorption, surface area exposed, and many other factors have an equal if not more important role in estimating mobilization of the listed elements.

The Galena subsite mineralization should not be compared to the unmined Flambeau sulfide ore body in Wisconsin. Mineralization at Galena is a Mississippi Valley massive sulfide type deposited in Late Paleozoic to Early Tertiary time, in a stable continental area, hosted in limestone, containing essentially two ore metals (approximately in the ratio of four zinc to one lead) and deposited at temperatures less than 120° Celsius. In contrast to the Flambeau which is a volcanogenic type massive sulfide, formed in areas of submarine volcanoes in pre-Cambrian time, containing copper, zinc, lead, silver, and gold as ore minerals deposited in volcanic host rocks at intermediate to high temperatures. Furthermore, the Flambeau deposit has been metamorphosed.

The Flambeau ore body contains approximately 60 percent pyrite, 12 percent chalcopyrite, (copper iron sulfide), 2.5 percent sphalerite and minor amounts of gold, silver, galena, and pyrrhotite. The Tri-State District (which the Galena subsite is part) ores produced 11,622,899 tons of zinc (sphalerite, smithsonite, calamine) and 3,131,715 tons of lead (galena, anglesite, and cerussite) (Ritchie, 1986). Marcasite and pyrite percentages are not reported. They are thought to be less

than 5 percent total. There may be a little chalcopyrite. Marcasite is the most common iron sulfide but microscopic pyrite is also common.

The two deposits have very little in common other than they are both massive sulfides.

P.21--Item 5. The amount of sulfuric acid produced depends on the amount of surface area of marcasite and pyrite exposed. The pH of both surface and ground water depends upon the amount of carbonate and to a lesser extent silicates available to buffer the water.

P.21--Item 6. It is acknowledged that there are carbonates peripheral to and associated with mineralization that can neutralize the pH but it must be recognized that this action may or may not reduce mobilization.

P.22 This idealized cross section is a concept based on only six wells, four of which are not located, in a depth range of 5 to 30m below surface. The analytical data is not tabulated and the author doesn't describe what ions were analyzed. The reviewer cannot evaluate independently the data. However, iron concentrations higher than sulfate concentrations are highly suspect. The high iron concentration and high pH indicates a reduced, not an oxidized, groundwater system. Given these differences, this data should not be compared with the Galena Subsite groundwater system.

P.23--Item 7. The phrase "immediate vicinity" requires quantification.

P.23 2nd paragraph under Shallow Groundwater, 1st sentence. "Everything indicates that it stood so during the period of ore deposition and during premining time." This statement needs documentation or reference with evidence for both the period of ore deposition and the premining time.

P.23 2nd paragraph, 2nd sentence. Haworth (1904) also states that heavy rainstorms caused complete abandonment of mining operations, some times for 3 to 4 weeks time (p. 96) and that roofs of mines usually were leaking water under large tailings piles while roofs some distance from the piles were dry (p. 99).

P.24 1st full sentence. It is difficult to judge what a trace amount of lead in spring water means. It may not be lead at all.

P.24 1st full paragraph, 2nd sentence. Absence of local gypsum deposits does not preclude the possibility that

gypsum could supply sulfate. Sulfate could also be supplied by secondary sulfate minerals.

- P.24 1st full paragraph, last sentence. Color alone is not a good judge of the presence of zinc carbonate in suspension in the spring water. Cream colored to nearly white waters could contain calcium carbonate or even aluminum oxide.
- P.24 2nd full paragraph, 1st sentence. Are there chemical analyses that indicate all of the waters showing these deposits probably contain zinc? Have "these deposits" been analyzed to demonstrate that they are zinc carbonate? These springs are around Joplin not in the Galena subsite.
- P.25 1st full paragraph, 1st sentence. Siebenthal seems to have been speculating upon the origin of the spring suspensions also.
- P.25 Table 1 With all the above discussion about zinc, these analyses don't include zinc.
- P.26 1st and 2nd sentence. Since none of the shallow groundwater analyses predate mining, it is not appropriate to state that they serve as a basis for characterizing the chemical quality in premining time?
- P.26 2nd paragraph. Again, these springs are in the Joplin area.
- P.27 1st full sentence. The scientific connection has not been demonstrated for sulfate. Increased sulfate concentrations may (not is) be related to the oxidation and subsequent leaching of sulfide ores.
- P.27 1st full paragraph, 2nd sentence. Neutralization by itself does not immobilize all metals.
- P.27 1st full paragraph, 3rd sentence. Large amounts of carbonate can occur naturally in ground water in almost every location.
- P.27 1st full paragraph, last sentence. There is no reason to believe that spring waters indicate a possible chemistry of local shallow groundwater systems prior to mining any more than shallow groundwater wells. The representativeness of either depends on their location and relationship to the shallow groundwater system.
- P.27 2nd paragraph. The single chert body discussed includes at least two major inliers of carbonate.

P.28 1st full sentence. Similar reactions could have been occurring (not undoubtedly occurring) in premining time. The amount of groundwater moving through the "flint areas" as opposed to through the limestone dominated areas outside the main ore zones in premining time is not known.

P.28 1st full paragraph, 1st sentence. The extent to which these processes were occurring in premining time is not known.

P.28 1st full paragraph, 1st sentence. Processes occurring in premining time may have contributed sulfates to surface and shallow groundwater. Contribution of free sulfuric acid and metallic sulfates are speculative.

2nd sentence. Water associated with chert could potentially be more acidic (if there were no carbonates) and could potentially contain more metals if they were acidic but how much water moved through the flint areas and the surface area of metal bearing minerals exposed to solution are more the issues than chert/limestone.

P.29, 30. No response needed.

CHAPTER 4--GEOTECHNICAL COMPARISONS

P.31 1st paragraph next to last sentence. Geochemistry and water chemistry are constantly evolving sciences. While some theories predominate, there are many differing scientific arguments as the science progresses. It is an oversimplification to say that all arguments are the same.

P.31 2nd paragraph, 1st sentence. Extensive areas of sulfide ore bodies is perhaps more correct than extensive ore bodies in the Galena subsite.

2nd sentence. All ore bodies contained sulfides but they also contained secondary minerals as well.

3rd sentence. The "laws of nature" are the same now as then. The geochemical reactions occurring are not necessarily the same near the Galena subsite sulfide ore bodies and those elsewhere in the world. Further, our understanding of the reactions has changed with time.

P.32 1st sentence. The basic premise of "large (10 to 20 percent) amounts of pyrite (FeS_2) and marcasite" is incorrect. It is about an order of magnitude too high. Marcasite and pyrite are generally not reported in the literature and are thought to be less than 5 percent total in this area.

3rd sentence. Marcasite and pyrite are not abundant in the Galena subsite of the Tri-State District.

4th sentence. Some to perhaps most references do mention the presence, distribution, and lack of abundance of these minerals. Sphalerite and galena are the most abundant minerals in the area.

P.32 2nd paragraph, 1st sentence. Again, pyrite and marcasite are not the most abundant sulfides present at Galena. Also, not all sulfides (e.g., sphalerite) are easily weathered.

P.33 1st full sentence. The oxidation of sphalerite does not lead to the formation of acid solutions. Certainly, the oxidation of every sulfide mineral does not lead to formation of acid solutions.

P.33 Equation in center of page. The reaction ignores the lead sulfate, which is the more likely precipitate. Anglesite may be more abundant than cerussite in the Galena subsite area (Ritchie 1986). Formation of lead sulfate or lead carbonate probably retards further oxidation.

P.34 Central full paragraph. This statement does not agree with Stewart's opinion verbally and in writing that there are no shear fractures or faults in the Galena subsite, only joints.

Last sentence in full paragraph. Which "ore deposits in geographic settings very similar to those that must have existed at Galena Kansas in the 1870's" are being referred to? Please supply a specific reference to facilitate comparative analyses.

P.35 3rd sentence. Agricola Lake is a volcanogenic massive sulfide (Archean metavolcanic rocks) not a Mississippi Valley type massive sulfide like the Tri-State District. It contains abundant pyrite and lead is probably immobilized as a lead sulfate. It is a very different ore type than that in the Galena subsite.

P.36 The Red Dog massive sulfide is a shale hosted type of massive sulfide. Shale hosted massive sulfides are deposited in rift basins (continents being pulled apart) with anomalously high thermal gradients with sulfides deposited as beds. They can be very large deposits (>30 million tons) and contribute up to 20 percent of the worlds silver production. A "typical" ore would be approximately 7 percent zinc, 3 percent lead, and 1.5 opt silver (also see discussion for P. 21-3 to contrast with Galena subsite). They also contain tens of percent

pyrite. The climate is one of permafrost, and no groundwater data is available in the EIS.

Linking the geochemical conditions at Red Dog with those of the Galena subsite is inappropriate.

- P.37 1st sentence. The situations at Red Dog and the situation of Short Creek are very different and not comparable (see above).

Last sentence in paragraph. What proof is there that the creek receives groundwater other than shallow (above permafrost) seeps? This condition is certainly not, nor could it have been prevalent, at Short Creek in premining time.

- P.37 Last sentence, most of p. 38. Please see discussion regarding Item 3 on page 21.

- P.38 1st paragraph, last sentence. Similar relations (to Figure 1) could not have prevailed in the Galena, Kansas, area water prior to initiation of mining because they are very different ore bodies in very different rock types, formed under different conditions and the data are open to question (e.g., Fe concentration being greater than sulfate concentration).

- P.38 2nd paragraph. Please refer to the previous discussion.

- P.38 Last sentence and top of p. 40. For all instances, all climatic and geologic settings, the groundwater/surface water interactions are not the same. Metals and their concentrations in waters are different from ore body to ore body even in the same massive sulfide type in different climates. Mobilization and transportation are related to the surrounding rock types with carbonates giving a very different spectrum of mobilization than volcanic rocks or metavolcanic rocks or shales. Many complex reactions need to be analyzed before making a general conclusion.

- P.39 Figure 1. Please see discussion of Figure 1, p. 22.

- P.40 1st full paragraph. We agree that weathering processes are the same and that they did occur at the ore deposits at Galena. The associated metals and their concentration transported in the groundwater and surface water were probably not the same due to variances in the extent of the reactions.

- P.41 First full sentence. The geologic formation (reviewers emphasis) outcrops on Short Creek. Mudge does not state that lead and zinc ores outcrop on Short Creek. If so,

they are certainly not evident today. Mudge does not mention the occurrence of pyrite or marcasite.

- P.42 Last sentence. There is no evidence that Short Creek water was even slightly acidic prior to mining. It is extremely unlikely that the creek ever contained lead and zinc in solution at least to the solubility limits of the minerals. Even today in the highest metals concentration in groundwater from abandoned mine shafts, these elements are not at their solubility limits as work being predicted by the thermodynamic relations.

This chapter like those prior to it ignore all geochemical reactions except idealized thermodynamic equilibrium calculations. This approach oversimplifies the natural setting to the extent that the concentrations calculated are maximum probable concentrations given infinite exposed fresh mineral surface and infinite time to equilibrate water concentrations with fresh surfaces.

CHAPTER 5--COMPUTER SIMULATION

- p.43 2nd paragraph, 1st sentence. This sentence is excellent and the following calculations have to be viewed in this perspective.

"Unfortunately, it is always difficult and sometimes impossible to determine such natural background concentrations after disturbances associated with mining and milling tend to uncover and expose metalliferous rocks and minerals of the region to natural processes of weathering and erosion." The only change this reviewer would make is change the "sometimes" to "almost always."

- p.44 1st paragraph, 3rd sentence. It is highly probable that the natural waters of the region may have contained some concentrations of some elements of concern but not necessarily elevated concentrations. Elevated concentrations imply an uncertain but potentially high concentration that will depend on location relative to mineralization and environmental conditions at that location.

Last sentence. Geochemical modeling is not particularly new, its power depends on its use, and it does not allow "going back in time."

- p.45 1st paragraph, 2nd sentence. Equilibrium-type geochemical models calculate an equilibrium concentration of a chemical element. It does not really calculate how much "should have dissolved" but calculates the affinity of either dissolving or precipitating a particular compound or mineral that contains specific chemical

elements. This affinity can be expressed as a thermodynamic "concentration" for specific chemical elements called activities. The actual concentration of any ion dissolved in water depends on many additional environmental factors in addition to thermodynamic equilibrium. However, equilibrium is a good beginning to see if a particular mineral or compound appears to be controlling the concentration of specific chemical elements.

- p.45 2nd paragraph, 3rd sentence. PHREEQE is widely used but there are several versions that have altered the original model either by adding minerals and/or compounds or by actually changing the code to give a specific output. Is the modeling code used in these calculations in its original state (Parkhurst and others, 1980) or has it been altered and what alterations have been made? No computer model has been "thoroughly" tested. Application of these solubility codes are really a continuing test of some thermodynamic data rather than an actual prediction of a dissolved concentration.

4th sentence. Thermodynamic models, like PHREEQE (WATEQ, MINTEQ, PATH, EQ3, etc.) are rapidly becoming working tools. PHREEQE is only one of several codes. WATEQ is also a U.S. Geological Survey code and is also widely use.

- p.45/46 PHREEQE does differ from other models in that it requires that the user choose the exact phases present during the reaction. If the user leaves some out that are present or puts some in that are not present, the model may not be able to calculate a correct affinity let alone activities of ions. The assumption of 10 to 20 percent pyrite in this case when the major iron sulfide is less than 5 percent total marcasite plus pyrite presents a significant difference in the phases present. Pyrite is observed only as microscopic crystals in the area of mining. Marcasite oxidizes at approximately half the rate of pyrite and is electrochemically more stable.
- p.46 1st full sentence. Is "the thermodynamic data base," that is both "large and appropriate," the original data base or has it been supplemented with additional or newer phases and/or equilibrium data? What criteria have been used to judge appropriateness of the thermodynamic data base for modeling the waters of the Tri-State District?
- p.46 Assumption (1) Another important question is what mineralogy is in contact with the natural waters. It is not very likely that the groundwater of the district

was in contact with enough of all the minerals to produce a equilibrium activity (not concentration) because even today with the increased exposure of sulfide mineralization the groundwater quality in the mine shafts, where peak concentrations have been observed, is below saturation with the mineralogy.

- p.46 2nd paragraph, 1st sentence. Since the major iron sulfide is marcasite and not pyrite, there is room for more discussion about adequate representation of the natural minerals. More discussion will be presented later when actual minerals are listed.
- p.47 Top paragraph, last sentence. The disequilibrium constraints such as redox reactions become very important when metal activities and adsorption reactions are to be considered. Factors such as order/disorder, crystal size (surface area), ionic substitution, and fresh versus aging precipitates become very important where the mobility of metals is concerned. Is the author assuming that the equilibrium "concentration" (or "maximum theoretical value") is the concentration of a metal ion to be expected across the Galena Subsite?
- p.49 Figure 1. The environments listed on this figure are idealized generalities. For example, not all mine waters have a pH <4 nor does all groundwater have an Eh ≤0.0. The use of this figure should be limited to a range of values be used in the calculations.
- p.50 2nd paragraph and later in the text and tables. Use of Eh values to 3 place accuracy is extremely misleading. Single digit accuracy is uncertain for this estimated parameter.
- p.50 2nd paragraph. The shallow aquifer in the Galena Subsite area is and has been in an unconfined condition essentially since the Pennsylvanian coal and shale series were eroded to its present condition. In its unconfined condition the shallow aquifer Eh is probably above zero due to exposure to atmospheric oxygen and infiltration oxygenated flows.
- Presence or absence of hydrogen sulfide gas cannot be used to justify the moderately- or strongly-reducing Eh for shallow or deep groundwater because it covers a Eh range of at least 600 millivolts (from approximately +0.3 to -0.3) and a pH <7.
- p.51 With both smithsonite (ZnSO_4) and anglesite (PbSO_4) associated with the ore these mineral phases should have been included in the list.

p.52 1st paragraph, 2nd sentence. Different combinations of these parameters are much more likely to yield a very different predicted final composition of the water at equilibrium--particularly for the metals if all phases are considered.

3rd sentence. We agree with this sentence. It displays the variability in modeling through the use of different input parameters. In this case we feel that some of these necessary inputs have been omitted from the analyses.

2nd paragraph, last sentence. It is correct to state that the analog could depict what might (not would) result from the equilibration of rain water with various assemblages of minerals.

p.53 1st full sentence. The data being described in this sentence needs to be presented. No simulations are shown that demonstrated that "concentrated ions of these metals would certainly have been put into solution." Is there a table missing? The calculations (simulations) would certainly have indicated an affinity to dissolve metals from the minerals but would certainly not demonstrate how much would be put into solution.

2nd sentence. It is not obvious that high concentrations of lead could easily have been present in Short Creek because lead sulfate is not included in the list of phases and also because lead is adsorbed on ferrihydrite at a pH greater than approximately 4.5. It is also either obvious nor clear that "high" concentrations of Zn and Cd could "easily" have been present in Short Creek. High should be defined.

3rd sentence. What evidence is there that the water is "naturally" acidic? Neutralization depends on the volume of acidic water relative to the volume of limestone and the amount of hydronium ions available to react. If extensive limestone is required, there must be either an extensive volume of acidic water or a large volume of very acidic and well buffered water.

p.55 1st paragraph, 1st two sentences. What was the criteria whereby "meaningful" assemblages of minerals were selected. The assemblage in the second sentence is not consistent with Ritchie, 1986, p.4, another of the author's references that lists only 11 minerals that are "common" selected from the approximately 40 minerals reported in the Tri State District. He (Ritchie) does not list pyrite as common. Of the 15 minerals the author listed hemimorphite (or calamine) is missing from the list and pyrite, millerite, greenockite, jarosite, barite, gypsum, and ferrihydrite are added. Are these additional minerals

to be considered common? If so, why is anglesite (PbSO_4) missing from an earlier discussion of lead solubility? Also, why is anglesite missing from the list of minerals on Table 1, the list of minerals used in "computer simulations?"

p.55 1st paragraph, 3rd sentence. It may "not be surprising to find these" compounds in association with the ore deposits but there is also numerous other intermediate compounds (like the common mineral hemimophite) and reactions that would reduce the metal ion concentration below that of a calculated thermodynamic equilibrium "concentration".

p.55 1st paragraph, last sentence. Anglesite is not on Table 1 but should have been included.

p.55 2nd paragraph, 1st sentence. What depth range is the author referring to as "deeper ground water"? Also, please define an undisturbed deposit.

p.56 1st full sentence. Is this a hypothetical situation or one that is being conjectured to represent the Galena subsite of the Tri State District? We need some rationale as to why the Eh and partial pressure of carbon dioxide values were "chosen" as being "reasonable" for "deep" (needs definition) ground water. The problems at Galena are in the shallow groundwater system.

p.56 4th full sentence. From the few results of the calculations reported in the text, one may not clearly conclude that a "deeper buried" limited sulfide mineralogy (not ore deposit) in the restricted conditions may not pose a "hazard to ground water." What does "any hazard to ground water" mean? This approach ignores the fact that the sulfide ore bodies in the Galena Subsite were associated with a siliceous replacement of a carbonate host rock. The sulfides were in a siliceous host rock not a carbonate.

p.56 1st full paragraph, 2nd sentence. Again, what is the rationale for designation of the Eh value? The calculated "dissolved Ni concentrations assumes millerite to be a very common mineral or that the volume of ground water is low. The author is assuming that the calculated potential thermodynamic values are dissolved concentrations. As discussed earlier, this may not be the case due to non-modeled factors.

3rd sentence. The calculated activities for the other heavy metals should be presented for completeness.

- p.57 1st full paragraph. Again, this assumes that the nickel mineral is common (abundant) which it is not, that activity equals dissolved concentration, and that other natural processes (adsorption, intermediate oxidation products, etc.) do not operate. Such ideal conditions do not exist in the natural conditions.
- p.57 2nd paragraph. What mineralogy is being used in this simulation and what are the other results? Four place accuracy (19,140 mg/l) is inappropriate considering that the calculation is only able to give affinity for the reaction to occur.
- p.58 Top of page, partial paragraph. The conditions discussed herein may be present for a brief (not geological) time when a host rock is fractured, exposing fresh sulfide to oxidation. A intermediate oxidation product will form slowing the oxidation of the metal sulfides. The extent of this reduction depends on the sulfide and the conditions. Mobilization of trace elements--transport into the groundwater system and removal from the site of oxidation--depends on many more natural processes than defined by simple thermodynamic affinity calculations which essentially assumes unlimited quantities of fresh metal sulfides exposed to an immobile aqueous phase long enough for equilibrium to be established and that all other phases have been identified and are similarly at equilibrium.
- p.58 1st full paragraph. "Severe natural contamination" requires definition.
- p.58 1st full paragraph, 4th sentence. The current data do not show equilibrium concentrations for the shallow groundwater, as one is lead to believe exist from the modeling.
- p.58 Last sentence. We do not concur that the author has used a conservative approach.
- p.59 2nd paragraph, 1st sentence. Again the calculated activity is not a real concentration and it is not "clear that enormous concentrations of dissolved metals could be produced" because of the over simplification of the natural system. On the previous page (P.58, paragraph 2), the author acknowledged lack of time for surface water to equilibrate.

The author should provide references for natural surface water samples that have a Eh of (+) 0.8 volts at a pH of 7.

- p.60 Top of page, 1st full sentence. The ore was not "discovered in surface outcrops" at Galena.
- p.60 2nd full paragraph under Interaction... The conditions and mineralogy described in this paragraph need more description before they can be expected to be accepted as "reasonable." Looking at Table 6 (p.62) referred to in this paragraph, the lack of lead and zinc sulfate minerals, for example, is not reasonable. The zinc silicate is missing. Why does the partial pressure of carbon dioxide change? The main host rock, silica, has been ignored.
- p.63 Top of page. These calculations do not "determine if it is possible to release meaningful concentrations of dissolved metals" by natural weathering and dissolution. See the above comments. The PHREEQE model does not calculate the actual concentration as admitted by the author in the first part of this sentence.
- p.63 2nd full sentence. Reference to Table 7 p.64. It is obvious from Table 7 that high concentrations of dissolved metals can be calculated to be possible--not that these concentrations could be produced under natural weathering conditions.
- p.65 The chemistry of Chico Spring 1st paragraph, 2nd sentence. Other springs in the region do not precipitate hydrozincite when they emerge from the ground.
- 3rd sentence. Again this method of calculation does not determine the "natural concentration" nor concentrations that "would have to be present."
- 5th sentence. The calculation estimates what may remain, not could remain in solution.
- 6th sentence. What criteria were applied to determine that Chico Spring "appears to be rather typical in composition"? Which springs were used for comparison?
- p.66 2nd full sentence. This may reflect ignored ions in the analysis and/or poor analytical data rather than a method of defining pH. Were other more recent analyses from the Galena Subsite area also used to calculate the pH in the same manner to compare with measured pH values?
- 3rd full sentence. Depth ranges "deeper" and "near surface" groundwater need to be defined.
- p.66 Precipitation of Hydrozincite. It has not been proven that the off-white precipitates reported to have been precipitating from selected springs in the area were in

fact hydrozincite. The references speculate that this was the case.

- p.67 Top of page. It remains to be demonstrated that attributing contamination to the mining activities is incorrect.
- p.67 Maximum Dissolved Concentrations. These are all calculated activities, not concentrations, that represent equilibrium values relative to a thermodynamic equilibrium value that in itself is subject to change. It is interesting that earlier calculations did not include the zinc silicate phase.
- p.69 Top of page. Consistent predictions may be the result of using the same mineral phases and equilibrium values. These calculated activities should not be used to judge anything more than the equilibrium values used in the calculation.
- p.69 Last sentence. We disagree with this conclusion. The modeling results are only one measure to be used to predict potential maximum, but not necessarily actual, concentrations before or after mining concentrations.

